

UNCLASSIFIED
SECURITY CLAS:

MASTER COPY

FOR REPRODUCTION PURPOSES

AD-A194 257

2

DOCUMENTATION PAGE

1. REPORT SEC Unc.	1b. RESTRICTIVE MARKINGS		
2a. SECURITY C	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) ARO 21827.4-CH	
6. NAME OF PERFORMING ORGANIZATION University of Southern Calif.	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) University Park Los Angeles, CA 90089-1661		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAG29-85-K-0015	
8c. ADDRESS (City, State and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. PROJECT NO. TASK NO. WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Aliphatic Nitrocompounds & Nitrated Reactive Intermediates			
12. PERSONAL AUTHOR(S) Olah, George Andrew			
13a. TYPE OF REPORT Final Report	13b. TIME COVERED FROM Nov.84 to Dec.87	14. DATE OF REPORT (Year, Month, Day) 1988, 2/17	15. PAGE COUNT 7
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Aliphatic nitration; nitronium salt nitration; desilylative nitration; nitrocarbenium ions.	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The electrophilic nitration of alkanes and cycloalkanes with nitronium salts was studied. Nitration of the cage hydrocarbon adamantane served as a particularly suitable model for these studies. Alkyl and allylsilanes were found to undergo desilylative nitration with nitronium salts providing a mild, selective method to introduce nitro groups into aliphatic compounds. The study of nitrated reactive intermediates, particularly nitrocarbocations was also carried out. The first stable α -nitrocarbocation, the diphenylnitrocarbenium ion, was prepared and characterized by ^1H , ^{13}C and ^{15}N nmr spectroscopy. The elusive nitrodiazonium ion was <i>in situ</i> prepared and its nitrating ability studied.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

APR 11 1988

DTIC
ELECTE

Aliphatic Nitrocompounds & Nitrated Reactive Intermediates**George A. Olah****March 17, 1988**

**U. S. ARMY RESEARCH OFFICE
P. O. Box 12211
Research Triangle Park, NC 27709-2211**

DAAG29-85-K-0015

**Hydrocarbon Research Institute
University of Southern California**

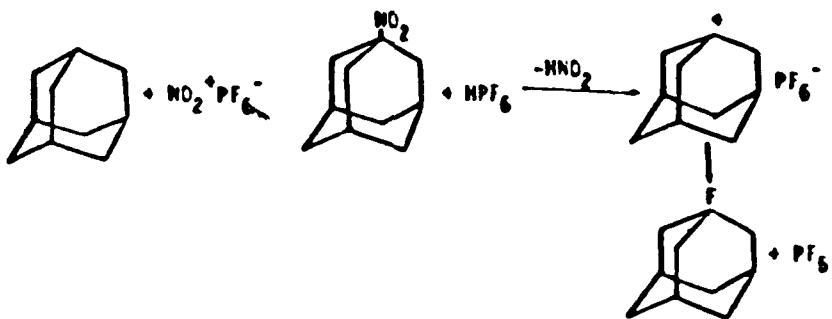
Classification	DAAG-29-85-1
Date	DAU 1988
Unlimited	<input type="checkbox"/>
Justification	<input type="checkbox"/>
By	
Distribution	
Availability Codes	
Mail and/or	
Other	Special
A-1	
C. INSPIRE	

**Approved for Public Release;
Distribution Unlimited.**

Electrophilic nitration of alkanes and cycloalkanes

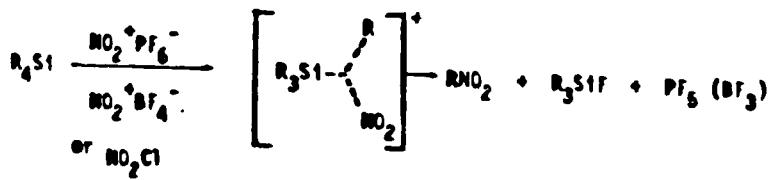
In the last three years our studies were directed to electrophilic aliphatic nitration of alkanes and cycloalkanes.

Initial studies of the electrophilic nitration of alkanes with nitronium salts was extended. Effects arising from the acid catalyzed cleavage reactions of tertiary and secondary nitroalkanes were investigated. This is considered the greatest preparative difficulty to adapt this novel, simple nitration method to practical use. Isobutane, for example, when nitrated with nitronium salts, nitrates predominantly on the tertiary C-H bond. 2-Methyl-2-nitropropane is, however, exceedingly sensitive to acid cleavage giving the *t*-butyl cation, which subsequently can deprotonate to give isobutylene and subsequently a multitude of side products. Whereas when using nitronium salts, the system is initially acid free, the substitution reaction, of course, generates an equimolar amount of strong acid. The same considerations are also valid for the nitration of adamantanone although in this case no olefin formation is possible. Tertiary 1-nitroadamantanone cleaves, however, very readily with acids to the 1-adamantyl cation, which can be then abstract halide ion from the counter ion or react with other nucleophiles.



The utilization of organometallics in preparing nitrocompounds has received so far little attention, except desilylative nitration of aryltrimethylsilanes.

We have found that tetraalkylsilanes react readily with nitronium salts according to the equation:



Tetramethylsilane with $\text{NO}_2^+ \text{BF}_4^-$ in sulfolane solution gives according to the reaction



nitromethane in 80% yield.

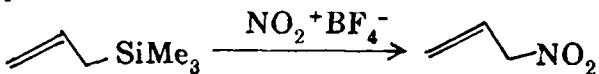
It is possible by using excess nitronium salt to carry further the reaction by reacting Me_3SiF itself



Me_2SiF_2 , however, does not react further.

Similar nitration of Et_4Si was observed and study was also extended to other alkylsilanes.

The reaction of allyltrimethylsilane with $\text{NO}_2^+ \text{BF}_4^-$ gave a >80% yield of 1-nitropropene-2

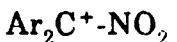


Whereas allylic nitration of the corresponding silanes proceeds well vinylic systems such as gave only polymers.

Study of nitrated reactive intermediates

An additional new aspect of our studies of the last three years was directed towards the study of nitrated reactive intermediates, particularly nitrocarbocations.

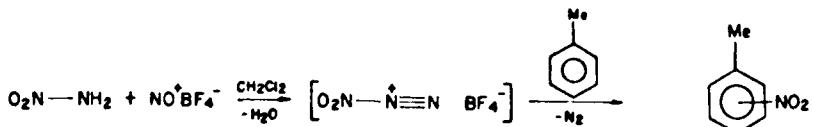
A detailed study of α -nitro diarylmethyl cations of the type



was carried out. These ions were successfully prepared from their corresponding gem-dinitro compounds in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ solution. Their structure was fully characterized by NMR (^1H , ^{13}C , ^{15}N) spectroscopy. Of particular interest was the evaluation of the effect of the α -nitro group on the carbocationic center.

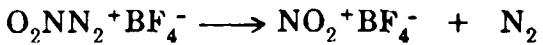
^{15}N NMR spectroscopic studies of solutions of nitric acid in various superacids were carried out in continued effort to probe the nature of nitrating agents in these media. In the course of our studies directed towards nitrated intermediates we have found that nitrodiazonium tetrafluoroborate $\text{O}_2\text{N}^+ \text{N} \equiv \text{N}^- \text{BF}_4^-$ can be

generated when nitramide is allowed to react with a molar equivalent of NO^+BF_4^- in CH_2Cl_2 at 0°C .



Dediazoniative nitration of toluene (4 equiv) gave isomeric nitrotoluenes in 36% overall yield. The observed isomer distribution of nitrotoluenes is 71% ortho, 3.5% meta, and 25.5% para and closely resembles that of electrophilic nitration of toluene with strongly electrophilic nitrating agents, such as nitronium salts.

In a control experiment when nitramide was added to dry toluene in CH_2Cl_2 under the experimental condition, no nitrotoluenes were observed after workup and GC analysis, ruling out any possible nitration of toluene by nitramide itself or by nitric acid formed upon hydrolysis. Dediazonation of the nitro diazonium ion to the nitronium ion is thermodynamically favorable and thus it cannot be excluded that its formation precedes nitration of aromatics.



Writing of Comprehensive Review of Nitration

During the last grant period a substantial effort was extended by the senior investigator in cooperation with his former colleagues, Dr. R. Malhotra and Dr. S. C. Narang (both with Stanford Research Institute) in writing a monograph entitled "Nitration: Preparative and Mechanistic Aspects". The book will give a critical review emphasizing both preparative and mechanistic aspects of aromatic and aliphatic nitration. Inevitable delays postponed completion but the manuscript is expected to be completed for publication in 1988.

Scientific Personnel Supported (in part) and Degrees Awarded:

George A. Olah, principal investigator
Judith A. Olah, co-principal investigator
Christophe Rochin, post-doctoral associate
Chandra B. Rao, post-doctoral associate
Judith Handley, graduate fellow
Joseph G. Shih, graduate student (Ph.D. 1985)

List of Publications under ARO Sponsorship: 1984-87

Olah, G. A., Prakash, G.K.S., Arvanaghi, M., Krishnamurthy, V. V., and Narang, S. C., α -Nitro diarylmethyl Cation. J. Am. Chem. Soc., **106**, 2378 (1984).

Olah, G. A.; Laali, K.; Farnia, M.; Shih, J.; Singh, B. P.; Schack, C. J.; Christie, K. O. Cyanation and Nitration of Toluene with Cyanamide and Nitramide through Intermediate Cyano- and Nitro diazonium Ions. Attempted Fluorination of Aromatics with Fluorodiazonium Ion, J. Org. Chem. **50**, 1338 (1985).

Olah, G. A., Pradeep, S. I., Prakash, G. K. S. Perfluorinated Resinsulfonic Acid (Nafion^R-H) Catalysis in Synthesis, Synthesis, 513 (1986).

Krishnamurthy, V. V.; Shih, J. G.; Olah, G. A. Unexpected Formation of 1,4,7-9-Tetrafluorodiamantane in the Reaction of 1,4,9-Tribromodiamantane with NO_2^+ BF_4^- / Pyridinium Polyhydrogen Fluoride (PPIIF), J. Org. Chem. **51**, 1354 (1986).

Olah, G. A., Shih, J. G., Prakash, G. K. S. Fluorine-Containing Reagents in Organic Synthesis in "Fluorine the First Hundred Years", Banks, R. E., Sharp, P.W.A. and Tallow, J. C. eds.; J. Fluorine Chem. **33**, 377 (1986).

Olah, G. A.; Yamato, T.; Hashimoto, T.; Shih, J. G.; Trivedi, N.; Singh, B. P.; Piteau, M.; Olah, J. A. Electrophilic Nitration, Halogenation, Acylation and Alkylation of α,α,α -Trifluoromethoxybenzene, J. Am. Chem. Soc. **109**, 3708 (1987).

Olah, G. A.; Rochin, C. Desilylative Nitration of Alkyl- and Allylsilanes with Nitronium Salts, J. Org. Chem. **52**, 701 (1987).